SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS POLY(SILOXANE-G-PIVALOLACTONE)

BY

DINESH VINAYAK PATWARDHAN

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

1991

कर्मण्येवाधिकारस्ते मा फलेषु कदाचन ॥
मा कर्मफलहेतुर्भूर्मा ते सङ्ग-ोऽस्त्वकर्मणि ॥४७॥

To action alone hast thou a right and never at all to its fruits; let not the fruits of action be thy motive; neither let there be in thee any attachment to inaction.

Srimad Bhagavadgita (2,47).

ACKNOWLEDGEMENTS

I thank Dr. Ken B. Wagener for the encouragement and guidance he has given me during difficult times in his friendly manner.

I thank Dr. James Deyrup and Dr. William Dolbier Jr. for serving on my committee and also the Army Research Office for their financial support of this work.

The pivalolactone used in this research was graciously donated by Dr. Gus Ibay, Southern Research Institute, Birmingham, Alabama.

Special thanks are due to Rudy Strohschein and R. W. Moshier for patiently listening to me and constructing glassware for me. Many thanks go to Chris Matayabas and Fabio Zuluaga for their excellent technical support and Kathy Novak for reading my manuscript. Also, thanks go to Lorraine Williams and Jane Poppell for helping me at all times. I am proud to have been a member of the University of Florida, Department of Chemistry, and the Center for Macromolecular Science and Engineering.

Words cannot express my gratitude towards my friends especially Amitabh and Bala.

Very special thanks go to my father and my mother for their blessings and to dear Chitra for her support. Without their encouragement I would have never reached this stage.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS iii
ABSTRACT v
INTRODUCTION 1
Graft Copolymers 1
The Selection Of Polydimethylsiloxane as a Backbone 6
Goals of This Research Work 7
EXPERIMENTAL 10
General 10
Chemicals and Instrumentation 11
Formation of the Five Polysiloxane Copolymer Backbones 12
Synthesis of (Silox)37-COOH: 12
Synthesis of (Silox)60-COOH: 13
Synthesis of (Silox)120-COOH: 14
Synthesis of (Silox)10-COOH: 14
Synthesis of (Silox)20-COOH: 15
Conversion of the Acid Appendage of the Backbone to the "Salt" 15
Synthesis of (Silox)37-COOK: 15
Synthesis of (Silox)60-COOK: 16
Synthesis of (Silox)120-COOK: 17
Synthesis of (Silox)10-COOK: 17
Synthesis of (Silox)20-COOK: 17
Grafting of Pivalolactone on to the Polysiloxane Backbones 17
Synthesis of (Silox)37-COO-(PVL)n Graft: 17
Synthesis of (Silox)60-COO-(PVL)n Graft: 18
RESULTS AND DISCUSSION 19
The Nature of the Graft Copolymer 19
Synthesis of the Polysiloxane Copolymer Backbone 20
Conversion of the "Acid" to the "Salt" [(Silox)n-Cook] 23
Drying of the "Salt": An Experimental Necessity 31
The Grafting Reaction 33
Conclusions 38
REFERENCES 39
BIOGRAPHICAL SKETCH 41

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS
POLY(SILOXANE-G-PIVALOLACTONE)

By

DINESH VINAYAK PATWARDHAN

December,1991

Chairman: Dr. Ken B. Wagener
Major Department: Department of Chemistry

The research in this thesis entails the synthesis and characterization of a series of graft copolymers with polydimethylsiloxane backbones to which are attached polypivalolactone grafts. The polydimethylsiloxane backbones contain pendant carboxylic acid groups as an active site for grafting. The backbones differ from each other in the number of these acid appendages per unit length, which means that the spacing between two consecutive grafting sites is different for all the grafts in the series. The polydimethylsiloxane backbones were synthesized via the hydrolytic co-polymerization of dimethyldichlorosilane (I) and 3-cyanopropylmethyldichlorosilane (II). The five different polydimethylsiloxane copolymer backbones were synthesized from five different ratios of the starting

silanes. These ratios were 10, 20, 37, 60 and 120 mmoles of the silane I to 1 mmole of the silane II. Further, these polydimethylsiloxanes with acid appendages were converted to their "salt" by two procedures:

a) The aqueous KOH method.

b) The dry KH method.

Both of these salt forming conversions are acid-base reactions, with the hydroxide ion and hydride ion being the base, respectively. The resulting salts were dried perfectly and then examined for the presence of any base before actual grafting was done with pivalolactone. These rigorous procedures were followed to avoid the formation of homopolypivalolactone. Further, two of these "salts" were grafted with pivalolactone to form the poly(siloxane-g-pivalolactone).

INTRODUCTION

Graft Copolymers

This thesis deals with the synthesis and characterization of a series of graft copolymers. According to the polymer science dictionary,[1] a graft copolymer consists of a backbone chain (polyA) to which are attached (one or usually more) graft chains of another polymer (polyB). A second definition, provided by IUPAC,[2] states that a graft copolymer is a high polymer which consists of two or more polymeric parts, of different composition, chemically united as opposed to a blend, which is just a physical mixture of two or more polymers.

In 1951 IUPAC formally accepted[2] the term "graft copolymer," and rules were established for its nomenclature. These rules state that the first polymer in the name represents the backbone, whereas the second polymer refers to the graft. For example, the name poly(siloxane-g-pivalolactone) means the backbone consists of polysiloxane, and polypivalolactone is grafted on it.

In the case of graft copolymers, it is usually the average length of the graft which is known. Also, only the average spacing between grafts can be calculated. On the

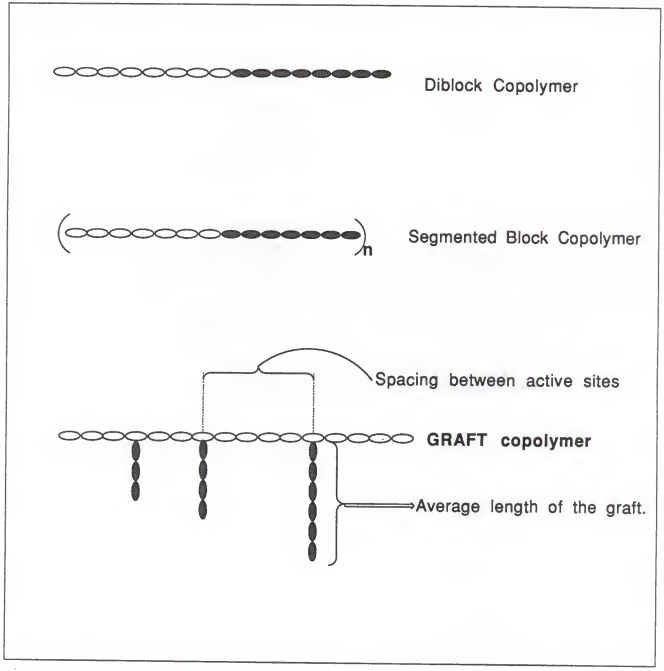


Figure 1 Depiction of Various kinds of graft and block copolymers

other hand in block copolymers not only is the length of the polymer chains accurately known, but it can be equal throughout the polymer. These differences[3] are depicted in Figure 1.

Why study these ambiguous graft copolymers per se when there are so many random copolymers and blends? The reason is that grafts offer other advantages. Incompatibility usually exists between two constituent polymers of a blend. This is because there is little to be gained from the free energy of mixing due to the length of the polymers involved. This incompatibility makes it very difficult to get a well dispersed polymer blend. On the other hand, a chemical bond exists between two polymers in the case of grafts. This chemical bond prevents the macroscopic separation although microscopic separation cannot be avoided. Also, grafts can be tailored accurately to suit specific applications, although synthesis of such tailored polymers is not easy.

Although there are many advantages of graft copolymers over blends and block copolymers, graft copolymers were neglected initially. This neglect was the result of problems faced in synthesis and characterization; the lack of reliable chemical methods of synthesis; the presence of solubility problems associated with grafts; the presence of homopolymers blended along with the graft copolymers; and not knowing accurate lengths of the grafts themselves.

In fact three methods of synthesis of graft copolymers have been clearly defined only recently, and they are as follows:[4]

a) The "Grafting from to" process,
b) The "Grafting on to" process and
c) The "Grafting through" process.

In the "grafting from to" process, an active center exists on the polymer where the monomer to be grafted is added in a chain propagation fashion, thus creating a grafted copolymer. In the "grafting on to" process, one of the polymer molecules carries one reactive site at the end of the chain, and another polymer, which has a reactive site randomly distributed along its chain, is grafted on to it. In this case grafting does not involve a chain reaction but is a simple attachment of two polymers at various points. This process has advantages, because each of the two polymers can be characterized separately before grafting is done. The last method, which has acquired attention recently, is the "grafting-through" process, whereby grafting is done on a macromer (a high molecular weight monomer). Figure 2 describes these three methods of synthesizing graft copolymers.

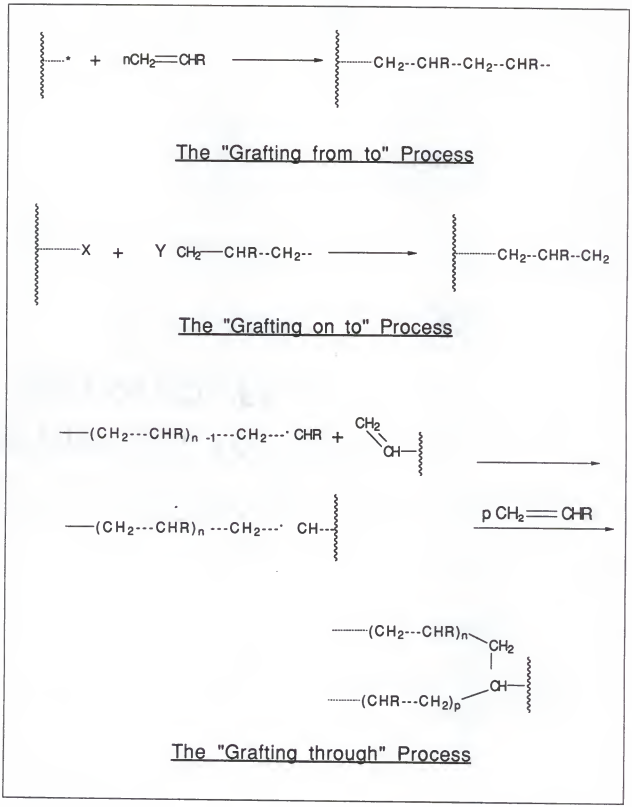


Figure 2. Three different methods for synthesizing graft copolymers

While these three methods of graft copolymer synthesis are known, problems remain. Even today the most widely used method for synthesizing graft copolymers involves the use of high energy radiation treatment (a "grafting from to" process) which does not give accurately tailored grafts for specific needs. Due to the lack of exact synthetic procedures for tailored grafts for specific use, there have been few applications. In recent years this situation has changed somewhat due to much better methods of characterization and other advances in synthetic methodology.

The Selection Of Polydimethylsiloxane as a Backbone

It is natural to develop interests in polydimethyl siloxane (PDMS) as the backbone for graft copolymers. This is due to the interesting properties[5] exhibited by polydimethyl siloxanes, such as their "organic-inorganic" nature. In addition, polydimethylsiloxanes have a low glass transition temperature (Tg); they are transparent to UV light; they have high permeability for gases, and they are film forming. The ionic character of Si-O bond makes it strong compared to the C-O bond. The methyl groups in PDMS can rotate around the Si-O bond very easily due to low cohesion forces. This rotation gives rise to flexibility which is one of the unique properties of polydimethyl siloxane. Because of this flexibility, the molecular weight of the polydimethyl siloxane must be very high for any mechanical strength to be achieved. This requirement can be satisfied by forming a

network polymer or by adding fillers like silica. Network polymers, however, are usually intractable and not processable and forming of graft copolymers would rectify this problem. The grafting of hard monomers like divinylbenzene,[6] styrene,[7] acrylamide,[8] methylmethaacrylate,[9] and polyurethanes[10] on a soft dimethyl polydimethylsiloxane backbone results in a graft copolymer with mechanically useful properties.

Such polymers are called thermoplastic elastomers. They contain a soft segment (segment having a tendency to be amorphous) and a phase separated hard segment (having a tendency to be semicrystalline). In these thermoplastic elastomers, the soft segment, which has a low glass transition temperature (Tg); segregates to form the amorphous soft phase, whereas the hard segment segregates to form a crystalline hard phase, which acts as a thermally labile physical cross link.

Goals of This Research Work

The research reported herein involves the synthesis of a series of five different polydimethylsiloxane (PDMS) backbones. Each of these backbones has a different number of the pendant carboxylic acid sites per unit length. The polydimethylsiloxane backbones were synthesized by the

hydrolytic polymerization of two dichlorosilanes, the ratio of which is given in Table I. These pendant carboxylic acid sites on the PDMS backbones then were converted to their "salts". Further, two of these salts were grafted with pivalolactone,[11] by a method which can be classified as a "from to process", to produce the graft copolymer. A concise scheme of this grafting procedure is given in Figure 3.

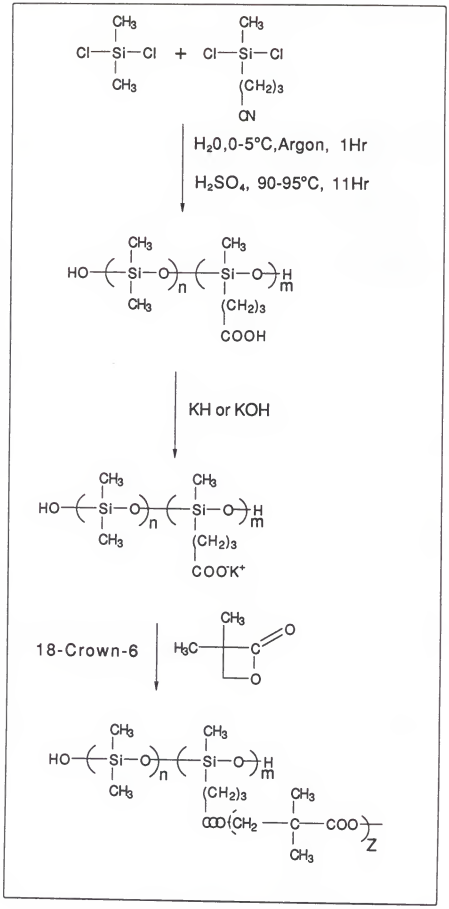


Figure 3. The complete synthesis scheme

EXPERIMENTAL

General

Two graft copolymers of poly(siloxane-g-pivalolactone) were synthesized, each with a different number of grafting sites, by polymerizing pivalolactone and the polysiloxane copolymer backbone, possessing pendant carboxylic acid functional groups. In addition three more polysiloxane copolymer backbones with a different number of carboxylic acid appendages per unit length were synthesized. Thus, a total of five copolymer backbones were synthesized. The polysiloxane copolymer backbone will be represented by $(Silox)_n$-COOH.

The five copolymer backbones were synthesized[12] via the hydrolytic copolymerization of dimethyldichlorosilane and 3-cyanopropyldimethyldichlorosilane in the presence of sulfuric acid. The molar feed ratio of the two monomers was 10,20,37,60, and 120 to 1. After the polymerization was complete, the copolymer was extracted with ether, and it was dried with magnesium sulfate. In each case the yield of $(Silox)_n$-COOH was about 40%. Each of the $(Silox)_n$-COOH backbone was characterized by ^1H NMR, which exhibited a singlet at 0.0 ppm for the methyl protons and multiplets at 0.5, 1.5 and 2.1 ppm due to the methylene protons. The

polysiloxane copolymer was also characterized by ^{13}C NMR and IR spectroscopy. All of the different $(Silox)_n$-COOH copolymers were then converted to their salt (represented by $(Silox)_n$-COOK) both by the aqueous potassium hydroxide method[13] or the dry potassium hydride method. Each salt, $(Silox)_n$-COOK, was thoroughly dried on a vacuum line and checked for neutrality. In the two cases when the grafting reaction was done, a homogeneous solution of the salt in THF was made first. About 0.01g of 1,4,7,13,16 hexaoxacyclooctadecane (henceforth will be represented as 18-Crown-6) was then added with continued stirring. An equivalent amount of freshly distilled pivalolactone was injected into the reaction mixture. The solution became heterogenous in 30 minutes. The reaction mixture was left in the dry box for 24 hours to complete the reaction. The graft copolymer was characterized by ^{1}H NMR and ^{13}C NMR.

Chemicals and Instrumentation

All solvents were reagent grade. Tetrahydrofuran(THF) was refluxed over a sodium and potassium alloy(2:1) overnight and stored under reduced pressure. Anhydrous diethyl ether was used directly from the container. The Argon which was used was dried by passing it first through sulfuric acid, then sodium hydroxide and finally through calcium sulfate. The chlorosilanes were purchased from Petrarch (Huls America) and used directly. Pivalolactone was graciously donated by

Dr. Gus Ibay from Southern Research Institute. It was dried over calcium hydride for 24 hours under reduced pressure and distilled just before use. The 18-Crown-6 ether was obtained from Aldrich and stored in the dry box, then used as-is.

Nuclear magnetic resonance data were obtained on Varian ™ XL-200 and XL-300 instruments, and all chemical shifts were reported in units of ppm using $CDCl_3$ as a solvent. Silanor-C was not used because the methyl protons give a peak at 0.00 ppm. The graft was dissolved in $CDCl_3$ and hexafluoro-isopropanol was added dropwise till the solution became clear (3 or 4 drops).

Infrared data were obtained using a Perkin Elmer ™-281 spectrophotometer with all results reported in units of Cm^{-1}.

Gel permeation chromatography (GPC) data for the siloxanes were obtained on the Waters 6000A Liquid chromatograph, equipped with a concentration sensitive differential refractometer detector.

Formation of the Five Polysiloxane Copolymer Backbones

Synthesis of $(Silox)_{37}$-COOH:

In a 3-neck round bottom flask, 50 ml of distilled water was added and Argon was used to flush the HCl out which would be formed during the reaction. To the central neck was attached an addition funnel containing 4.77g (37mmoles) of dichloro-dimethylsilane and 0.1820g (1mmoles) of 3-

cyanopropyl-methyldichlorosilane in 50 ml of anhydrous diethyl ether. Addition was done dropwise with the temperature maintained between 0-5°C. The stirring was continued for over an hour after which low molecular weight polymer with nitrile appendage was then extracted with ether. The yield was about 40%. The ether then was evaporated to isolate the oligomer. To the pure oligomer 50ml of 50% sulfuric acid was added and the reaction mixture was then stirred for about 11 hours maintaining the temperature at 90°C. The reaction was then purged with ice-cold water. The polysiloxane copolymer, $(Silox)_n$-COOH, was then extracted with ether and dried over magnesium sulfate.

The product analysis gave the following results:

^1H NMR($CDCl_3$): 0.0 (s, 6xn H), 0.5(m, 2H), 1.5(m, 2H)
2.1(m, 2H) ppm.

^{13}C NMR($CDCl_3$): 0.0, 16.2, 21.4 ppm.

IR(NaCl plates):3690, 1740-1700, 1160-1050(big band) cm^{-1}

Synthesis of $(Silox)_{60}$-COOH:

The procedure was as above except, 7.74g (60 mmoles) of dimethyldichlorosilane and 0.1820g (1 mmoles) of 3-cyanopropylmethyldichlorosilane in 50ml of anhydrous diethyl ether were used.

The product analysis gave the following results:

^{1}H NMR($CDCl_3$): 0.0 (s, 6xn H), 0.5(m, 2H), 1.5(m, 2H), 2.1(m, 2H) ppm.

^{13}C NMR($CDCl_3$): 0.0, 16.2, 21.4 ppm.

IR(NaCl plates):3690, 1740-1700, 1160-1050(big band) cm^{-1}

Synthesis of $(Silox)_{120}$-COOH:

The procedure was as above except, 15.48g (120 mmoles) of dimethyldichlorosilane and 0.1820g (1 mmoles) of 3-cyanopropylmethyldichlorosilane in 50ml of anhydrous diethyl ether were used .

The product analysis gave the following results:

^{1}H NMR($CDCl_3$): 0.0 (s, 6xn H), 0.5(m, 2H), 1.5(m, 2H), 2.1(m, 2H) ppm.

^{13}C NMR($CDCl_3$): 0.0, 16.2, 21.4 ppm.

IR(NaCl plates):3690, 1740-1700, 1160-1050(big band) cm^{-1}

Synthesis of $(Silox)_{10}$-COOH:

The procedure was as above except, 1.29g (10 mmoles) of dimethyldichlorosilane and 0.1820g (1 mmoles) of 3-cyanopropylmethyldichlorosilane in 50ml of anhydrous diethyl ether were used .

The product analysis gave the following results:

^{1}H NMR($CDCl_3$): 0.0 (s, 6xn H), 0.5(m, 2H), 1.5(m, 2H), 2.1(m, 2H) ppm.

^{13}C NMR($CDCl_3$): 0.0, 16.2, 21.4 ppm.

IR(NaCl plates):3690, 1740-1700, 1160-1050(big band) cm^{-1}

Synthesis of $(Silox)_{20}$-COOH:

The procedure was as above except, 2.58g (20 mmoles) of dimethyldichlorosilane and 0.1820g (1 mmoles) of 3-cyanopropylmethyldichlorosilane in 50ml of anhydrous diethyl ether were used .

The product analysis gave the following results:

^{1}H NMR($CDCl_3$): 0.0 (s, 6xn H), 0.5(m, 2H), 1.5(m, 2H), 2.1(m, 2H) ppm.

^{13}C NMR($CDCl_3$): 0.0, 16.2, 21.4 ppm.

IR(NaCl plates):3690, 1740-1700, 1160-1050(big band) cm^{-1}

Conversion of the Acid Appendage of the Backbone to the "Salt"

Synthesis of $(Silox)_{37}$-COOK:

The $(Silox)_{37}$-COOH was then converted to its salt either by the aqueous KOH or the dry KH method.

About 5g of $(Silox)_{37}$-COOH was dissolved in 500 ml of ether and taken into a separatory funnel; 10ml of 10M KOH was added to it, and the mixture was shaken for five minutes.

Excess KOH precipitated as a white salt. The $(Silox)_n$-COOH which was now a salt, $(Silox)_n$-COOK, was washed several times till it was neutral. A large excess of ether was always present to avoid formation of emulsion. The yield was about 90%. The ether was evaporated and the salt dried thoroughly on a high vacuum line for 24 hours.

In the second method the salt was formed with dry KH. The approximate number of carboxylic acid end-groups was first calculated by ^1H NMR to be $3.3x10^{-4}$ moles/g (which corresponds to 0.0132g of KH /g of polymer). Approximately 0.0132 of KH was taken in a preweighed three neck round bottom flask. It was washed with ether to get rid of mineral oil (which comes along with KH in the commercial package). The flask was weighed again to calculate the exact amount of KH. A corresponding amount of $(Silox)_{37}$-COOH was then added along with 100ml of ether. The reaction mixture was stirred for 6 hours under Argon. The product was analyzed by IR to check for the absence of Carbonyl peak at 1700 cm^{-1}.

Synthesis of $(Silox)_{60}$-COOK:

Both of the procedures described above were followed. The product analysis gave the following results:

IR (NaCl plates): 3690, small peak at 1650-1550, 1160-1050 cm^{-1}.

Synthesis of $(Silox)_{120}$-COOK:

Both of the procedures described above were followed. The product analysis gave the following results:

IR (NaCl plates) : 3690, small peak at 1650-1550, 1160-1050 cm^{-1}.

Synthesis of $(Silox)_{10}$-COOK:

Both of the procedures described above were followed. The product analysis gave the following results:

IR (NaCl plates): 3690, small peak at 1650-1550, 1160-1050 cm^{-1}.

Synthesis of $(Silox)_{20}$-COOK:

Both of the procedures described above were followed. The product analysis gave the following results:

IR (NaCl plates): 3690, small peak at 1650-1550, 1160-1050 cm^{-1}.

Grafting of Pivalolactone on to the Polysiloxane Backbones

Synthesis of $(Silox)_{37}$-COO-$(PVL)_n$ Graft:

In a dry box, about 2g of well dried salt was taken in a 3-neck flask and stirred with a mechanical stirrer along with 10-15 ml of THF until a homogeneous solution was obtained. Then 0.01 g of 18-crown-6 was added with continuous stirring. Two grams of freshly distilled pivalolactone then was added

to the solution. The reaction mixture became heterogeneous in 30 minutes, but stirring was continued until the reaction mixture became viscous. The reaction mixture was left in the dry box for 24 hours, after which it was washed with methylene chloride and m-cresol. The product was then dried and the analysis gave the following results:

^{1}H NMR: 0.0, 1.2, 4.0 ppm.

^{13}C NMR: 21.4,42.4,176.5 ppm.

Synthesis of $(Silox)_{60}$-COO-$(PVL)_n$ Graft:

The procedure used was the same as above. The product analysis gave the following results:

^{1}H NMR: 0.0, 1.2, 4.0 ppm.

^{13}C NMR: 21.4,42.4,176.5 ppm.

RESULTS AND DISCUSSION

The Nature of the Graft Copolymer

This project deals with the synthesis of a new series of graft copolymers possessing a polysiloxane backbone with polypivalolactone grafts. The polysiloxane copolymer backbone contains pendant carboxylic acid groups as active sites for pivalolactone grafting. The polysiloxane copolymer backbones differ from each other in the number of active sites per unit length which means that the spacing between two consecutive grafting sites is different for all the grafts in the series. Figure 4 shows a representative polysiloxane copolymer backbone with an acid appendage; this backbone will be denoted by $(Silox)_n$-COOH.

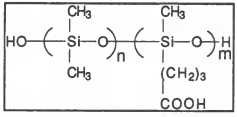


Figure 4. The polysiloxane copolymer backbone.

Further, the project deals with the conversion of two of these polysiloxane backbones to their graft copolymers by

grafting the backbone with pivalolactone. Figure 5 gives an illustration of the nature of the graft copolymer backbone.

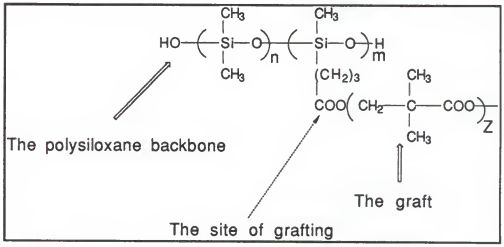


Figure 5. The graft copolymer.

Synthesis of the Polysiloxane Copolymer Backbone

Two dichlorosilanes, namely dimethyldichlorosilane(I) and 3-cyanopropylmethyldichlorosilane(II), were copolymerized in order to synthesize this series of polysiloxane backbones. Table I gives the five different ratios of the silanes used for synthesizing these siloxane copolymers. The first step in this synthesis, shown in Figure 6, involves hydrolytic polymerization, where two dichlorosilanes are added to water dropwise, thereby evolving hydrochloric acid. A strong argon flow is necessary to remove the HCl. After the chlorosilanes are added, stirring is continued for a little more than an hour to obtain sufficiently high molecular weight cyclics

Table I. Ratios of the dichlorosilanes monomers used to form the copolymer backbone.

mmoles of I	mmoles of II
10	1
20	1
37	1
60	1
120	1

such that extraction with ether is possible. The temperature is maintained at 0-5°C with an ice-bath, as this reaction is exothermic.

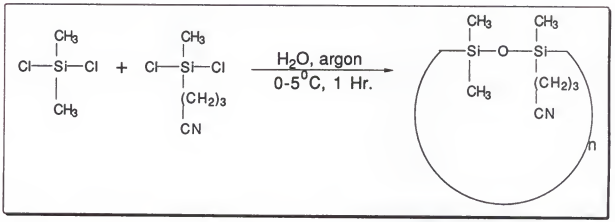


Figure 6. The formation of low molecular weight cyclics.

The next step[12], shown in Figure 7, is the most crucial one, where these cyclics with nitrile appendages are hydrolyzed to a high molecular weight polymer possessing

carboxylic acid appendages. The duration of the reaction influences both the percentage conversion of the nitrile appendage to the carboxylic acid appendage, and the molecular weight of the polysiloxane copolymer backbone. If the reaction time is long enough such that all the nitrile functional groups are converted to the carboxylic acid functional groups, then a high molecular weight, intractable polymer is obtained. On the other hand, if the duration of the reaction is shortened, then all the nitrile functional groups are not converted to carboxylic acid functional groups. The reaction time which was selected was such that a maximum percentage conversion of nitrile functional groups to carboxylic acid functional groups would be obtained without producing an intractable copolymer. An excess of sulfuric acid helps with this conversion. The reaction can be followed by infrared spectroscopy (IR) which shows the nitrile group at 2250 cm^{-1} being converted to a carboxylic acid group at 1700cm^{-1}.

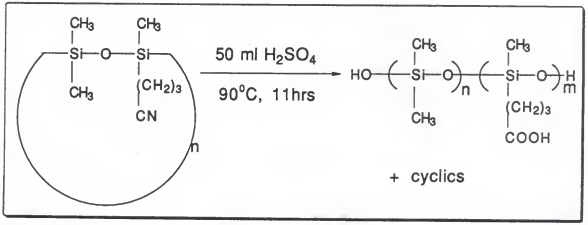


Figure 7. The formation of the polysiloxane backbone.

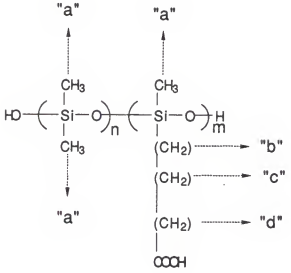
The reaction mixture is purged with ice-cold water. The polysiloxane copolymer, which is now a colorless, thick, viscous liquid, is extracted with ether and then washed with water to remove excess sulfuric acid. The $(Silox)_n$-COOH solution in ether is then dried over magnesium sulfate. Characterization of the $(Silox)_n$-COOH was done by ^1H NMR (Figure 8), ^{13}C NMR (Figure 9), IR (Figure 11) and gel permeation chromatography (GPC) (Figure 10). The proton NMR spectrum shows a singlet at 0.00 ppm for the methyl protons and three multiplets at 0.5, 1.5 and 2.0 ppm for the methylene protons. A ^{13}C NMR shows a peak for methyls at 0.00 ppm and the carbonyl stretching can be seen at around 1700 cm^{-1} in the IR spectra. The GPC data indicates that the chemistry involved is equilibrium step chemistry.

Conversion of the "Acid" to the "Salt" [$(Silox)_n$-Cook]

In the next synthetic step, the carboxylic acid appendage is converted into the "salt". Two procedures were followed; as represented in Figure 12.

a) The aqueous KOH method, and,

b) The dry KH method.



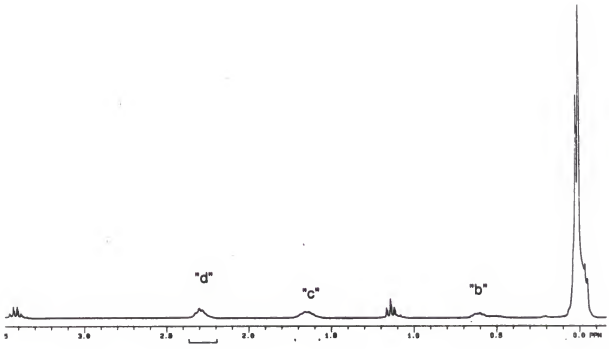


Figure 8. Representative ^{1}H NMR of the $(Silox)_n$-COOH. This sample is 37 mmoles to 1mmoles of the dimethyldichlorosilane to 3cyanopropylmethyldichlorosilane.

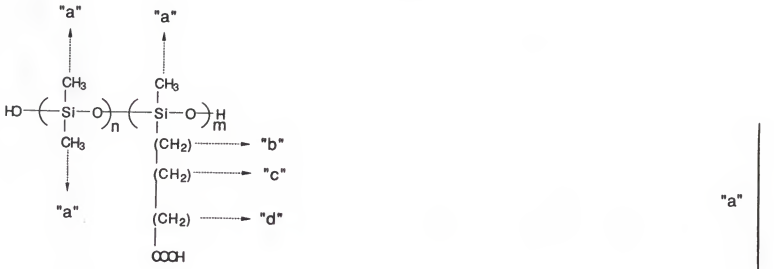


Figure 9. Representative ^{13}C NMR of the $(Silox)_n$-COOH. This sample is 37 mmoles to 1mmoles of the dimethyldichlorosilane to 3cyanopropylmethyldichlorosilane.

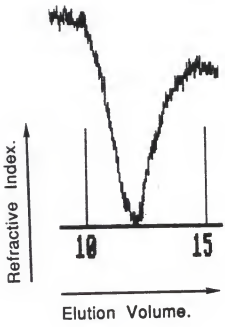
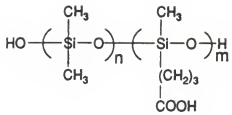


Figure 10. GPC curve for the $(Silox)_n$-COOH



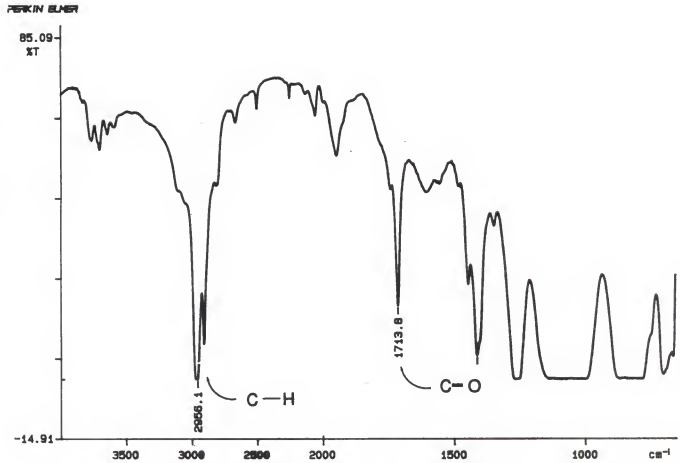


Figure 11. IR spectra of the (Silox)n-COOH of the 37:1 sample

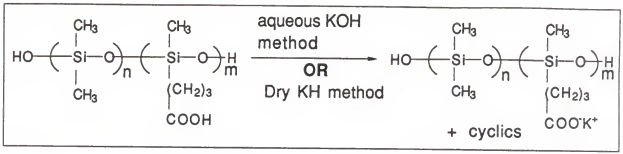


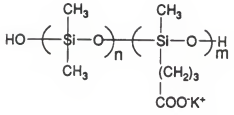
Figure 12. The conversion of the "acid" to the "salt".

These two methods are described below:

a) The Aqueous KOH method: The aqueous KOH method[13] is a two phase acid-base reaction. Concentrated potassium hydroxide in water is shaken with the solution of siloxane copolymer in ether, and the excess KOH precipitates as a solid. The salt, $(Silox)_n$-COOK, is washed with water several times to remove excess base. The ether, which also contains water, is dried by several means. First, magnesium sulfate is used, followed by toluene, which is added to form an azeotrope. This azeotrope is then evaporated. Finally, the salt is freeze dried on a vacuum line for 24 hrs with benzene as the solvent. The flask stopcock is then closed to keep the salt from being exposed to air. The salt, which is initially milky white in appearance, becomes clear after it is perfectly dry and neutral. Thus, a dry salt has beensynthesized for further conversion to a graft copolymer. The conversion of the carboxylic acid to the salt is observed by IR spectroscopy (Figure 13) where the carboxylic acid peak

at 1740-1700 cm^{-1} is shifted to the very small peak at 1650-1550 cm^{-1}. There is no other difference in the IR spectra of the acid and the salt, especially the hydroxy absorption[14] at around 3500cm^{-1}, indicating that only the carboxylic acid groups are converted to the salt. The end hydroxy groups are left untouched so they cannot act as a site for grafting. The overall yield in this conversion is around 90% because some cyclics are formed. These cyclics are formed because of redistribution and equilibration reactions which have been reported in the past.[15,16]

b) The KH method: The second method, also represented in Figure 12 is an acid-base reaction as well, where the hydride ion acts as a base and abstracts a proton from the carboxylic acid to form gaseous hydrogen. This method requires the calculation of the approximate number of carboxylic acid groups involved in this chemistry. Approximately the same equivalent number of moles of potassium hydride are used in the conversion. Calculation is required to avoid the addition of excess potassium hydride. The reaction is followed by IR to see the disappearance of the carboxylic acid peak at 1700cm^{-1} and the appearance of a small peak at around 1650-1550cm^{-1}. A typical reaction would take 5-6 hours, at the end of which no potassium hydride remains behind if the initial equivalence is accurate.



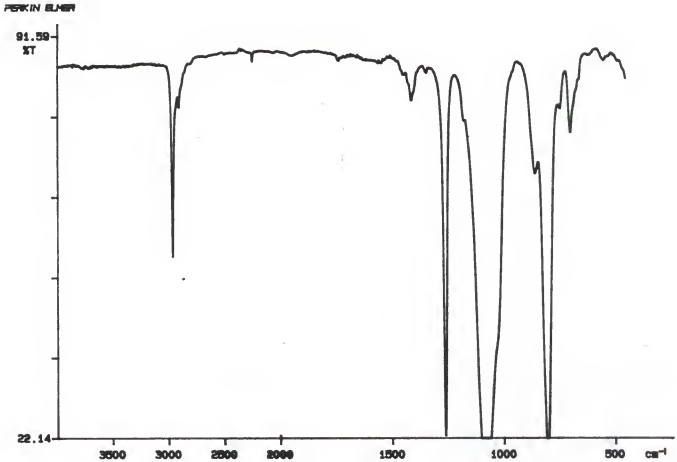


Figure 12. IR spectra of the "Salt" of the sample 37:1

Drying of the "Salt": An Experimental Necessity

The synthetic procedure at hand is such that the salt, $(Silox)_n$-COOK, must be perfectly neutral and dry before the grafting reaction with pivalolactone. If water or base is present, then the nucleophilic attack of hydroxide ion or water produces homopolypivalolactone. If this reaction is allowed to occur, then the result would be a "blend" of homopolymers of the two polymers involved instead of the formation of a graft copolymer. This side reaction is represented as in Figure 14.

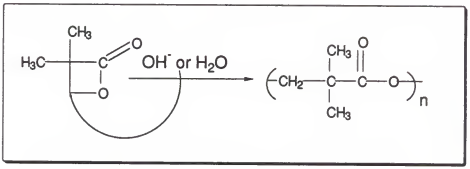


Figure 14. A side reaction producing homopolypivalolactone.

If the salt $(Silox)_n$-COOK is synthesized by the aqueous method, then emulsions are formed because of enhanced solubility of the "salt" in water due to the polar appendage. These emulsions make the situation slightly complex, because removal of both base and water is absolutely necessary, and this is difficult to accomplish in the presence of emulsions. The emulsion formation can be minimized by combining a small

amount of the salt with a large excess of ether, but emulsion formation cannot be avoided altogether. Extra care has to be taken through the extensive process of drying, first with magnesium sulfate, followed by azeotropic drying with toluene, and finally freeze drying with benzene. After completing these steps, a salt capable of grafting is produced.

If the salt is synthesized by the KH method, then excess hydride also can create a problem in the synthetic procedure on hand. This is due to the fact that it is very difficult to have an exact equivalence of KH to $(Silox)_n$-COOH. Therefore this salt, $(Silox)_n$-COOK, which does not have water, as is present in the previously described procedure, may have traces of unreacted hydride ion. Secondly, the carboxylic acid which is used for the reaction with KH may have traces of water which can react with KH to give a base, KOH. This hydride ion or the hydroxide ion would prevent graft formation and instead would ring open pivalolactone to give homopolypivalolactone (Figure 15).

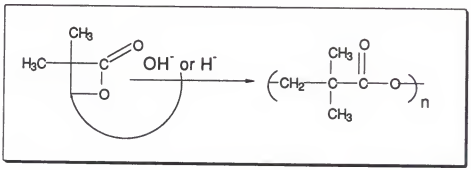


Figure 15. A side reaction producing homopolypivalolactone.

Water contamination can be avoided by using an absolutely dry carboxylic acid solution for the reaction with KH. The other reaction, in which excess hydride can be a problem, is avoided by providing a slight excess of the original carboxylic acid, $(Silox)_n$-COOH, solution in ether after the initial reaction. Any traces of KH react with acid, thus destroying it. The "salt" is then freeze dried with benzene as the solvent and is then left to dry on the vacuum line over night.

The Grafting Reaction

The "salt," dried by one of the methods discussed above, is taken to a dry box where the actual grafting reaction is carried out (Figure 16). Meanwhile pivalolactone is kept stirring under reduced pressure over calcium hydride overnight, and it is then distilled and taken into the dry box. A solution of 18-Crown-6 made in THF is also taken into the dry box along with a mechanical stirrer. About 2 g of salt is taken in a round bottom flask; THF is added to it, and it is stirred until a homogeneous solution is formed. The addition of about 0.01 g of 18-Crown-6 helps the dissolution of the salt. It also acts as a trap for the counterion,

potassium, thus increasing nucleophilicity of the carboxylate to initiate grafting. At this point 2g of pivalolactone is injected into the reaction mixture. The stirring is vigorous, and after about half an hour the reaction mixture becomes heterogenous. The stirring is continued until the mixture becomes quite viscous. This reaction represents a rare situation, in that the grafting continues even after the reaction mixture becomes heterogeneous. It is kept in the dry box for 24 hours until the reaction is complete.

In a control experiment it was shown that the crown ether by itself does not polymerize pivalolactone. Also, the acid in the presence of crown ether does not polymerize pivalolactone. This confirms that hydroxy end groups are much slower initiators than the carboxylate functional groups for pivlolactone polymerization.[17] After 24 hrs the reaction mixture is washed with m-cresol, a good solvent for homopolypivalolactone, and methylene chloride, a good solvent for polysiloxanes. The graft copolymer does not dissolve in any organic solvent alone; it dissolves only after the addition of 3-4 drops of hexafluoroisopropanol.

The ^{1}H NMR (Figure 17) of the graft shows a signal at 0.00 ppm due to methyl hydrogens in the backbone, a signal at 1.2 and 4.0 due to "b" and "c" protons. The ^{13}C NMR (Figure 18) shows signals at 21.4, 42.4, and 176.5 ppm.

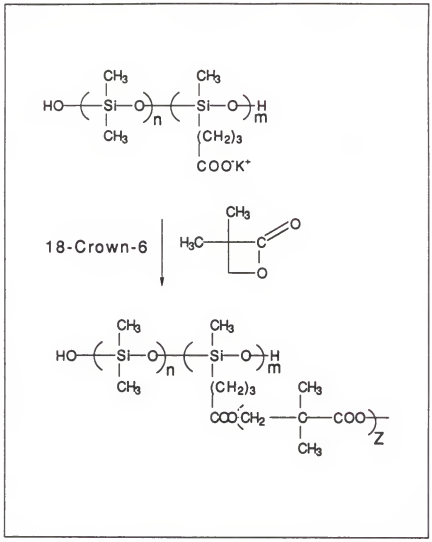


Figure 16. The Grafting reaction

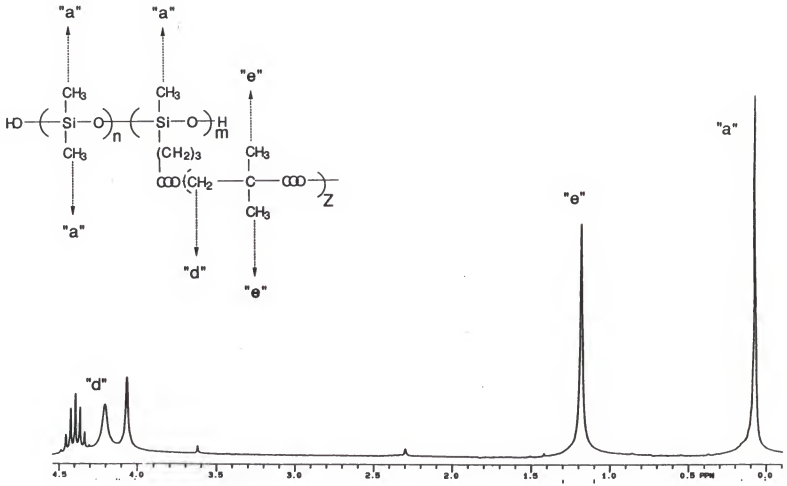


Figure 17. Representative ^{1}H NMR of graft copolymer. The ratio of the chlorosilane in the polysiloxane backbone is 37:1.

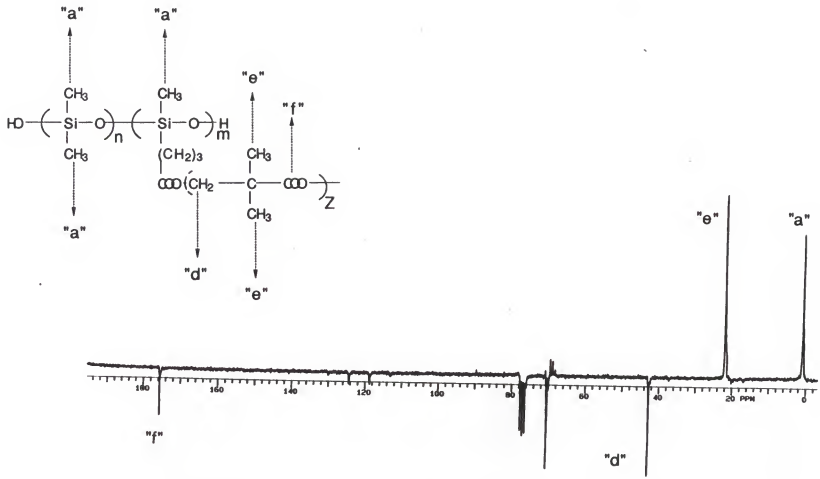


Figure 18. Representative ^{13}C NMR of graft copolymer. The ratio of the chlorosilanes in the polysiloxane backbone is 37:1.

CONCLUSIONS

Five polysiloxane copolymer backbones were synthesized from five different ratios of dichloromethyldimethylsilane and 3-cyanoproylmethyldichlorosilane via hydrolytic polymerization. These polysiloxane copolymer backbones have different numbers of appendages per unit length. These acid appendages were converted to their salts by two methods. The first method involved the reaction of aqueous potassium hydroxide as the base, and the second method involved the use of potassium hydride as the base. The salt, which was produced by either of these two reactions, must be perfectly dry and neutral before reacting with pivalolactone in order to avoid the formation of a blend of homopolymers. The nucleophilicity of the salt was increased by the presence of 18-crown-6 which complexed the potassium counterion. In two cases, pivalolactone was then grafted on the backbone.

These graft copolymers are thermoplastic elastomers having a soft segment of polydimethylsiloxane and a hard segment of polypivalolactone. Due to the vast difference in the glass transition temperatures (Tg) of the two components, these graft copolymers have a large operating temperature range. The crystalline state of the hard segment also enhances the solvent resistant properties and ultimate strength of the copolymers themselves.

REFERENCES

1. Alger M.S.M., Polymer Science Dictionary, Elsevier Applied Science, NY, 1989, 192.

2. Battaerd H. and Tregear G.W., Graft Copolymers, Wiley (Interscience), NY, 1967, 10.

3. Cowie John, in Comprehensive Polymer Science, Geoffrey Allen, EDS, Pergamon Press, NY, 1989, 3, Chapter 3, 34.

4. Remp P.F, Lutz P., in Comprehensive Polymer Science, Geoffrey Allen, Ed, Pergamon Press, NY, 1989, 6, Chapter 12, 403.

5. McGrath J.E., Yilgor I., in Advances in Polymer Science, Springer Verlag, Berlin, 1984, 86, Chapter 1, 6.

6. Midland Silicones, Brit Pat. #766,528, 1957.

7. McGrarth J.E., Dwight D.W., York G., Smith S.D., in Chemical Reactions on Polymers, Judith Benham, Ed., ACS Symposium Series, NV, 1988, Chapter 7, 85.

8. Warrick E. , US Pat. #2,959,659, 1956.

9. Nowak P., Ger. Pat. #1.134.834, 1962.

10. Yasuyuki T., et al. Polymer, 1989, 30, 553.

11. Jerome R., Teyssie' P., in Comprehensive Polymer Science, Geoffrey Allen, Ed., Pergamon Press, NY, 1989, 3, Chapter 34, 501.

12. Katyama Y., Kato T., Ohyangi M., Naruse H., Ikeda K., Sekine Y., Macromolecule Chem., Rapid Communication, 1986, 7, 153.

13. Wanigatunga S. and Wagener K.B., Macromolecules, 1989,22, 4155.

14. Smith A.L., Analysis of Silicones, Wiley(Interscience), NY, 1974, 275.

15. McGrath J.E., Riffle J.S., Banthia A.K., Yilgor I., Wilkes G.L., An Overview of the Polymerization of Cyclosiloxanes, Initiation of Polymerization, F.E. Bailey Jr, Ed., ACS Symposium 1983, 212, 150.

16. Grubb W.T., Osthiff R.C., JACS, 1954, 77, 1405.

17. Thamm R.C., Buck W.H., J Poly Sci. 1978, 15, 539.

BIOGRAPHICAL SKETCH

Dinesh V. Patwardhan was born in Bombay, India, on September 13, 1965. He lived most of his life in Bombay where he went to a locally known school, King George. He represented the school in general knowledge quizzes and chess.

After completing his high school education he went to the prestigious Ruparel College for further education until graduation, to obtain a B.Sc. in chemistry in 1985. In Ruparel college he organized cultural events and wrote for the college magazine.

In 1985 after finishing his B.Sc., he joined the well known Institute of Science, Bombay. He continued his writing and organization of cultural events. In addition he was active in local student politics. During the same period he was working on a project on ferrites under the supervision of Dr. V. S. Darshane.

In 1987 after finishing the M.Sc., he worked as a student trainee with CMC, a Government. of India Enterprise, for about 10 months. Here he learned Turbo PASCAL and BASIC languages.

In August of 1988 he came to the USA for the first time and due to the sudden changes, life was difficult for a short period of time. He joined Dr. Wageners group in May 1989.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Kenneth B. Wagener, Chairman
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

James Deyrup
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

William Dolbier Jr.
Professor of Chemistry

This thesis was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Master of Science.

Dean, Graduate School

December 1991